Density Functional Theory (DFT) Calculations on the Structures of 2:1 Clay Minerals

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RESEARCH OBJECTIVES

The objectives of this project are: (1) to assess the validity of our DFT calculations by determining the equilibrium structure of the clay mineral pyrophyllite, and (2) to determine the structure of the clay mineral Na-montmorillonite with varying layer charge created by $Al^{3+} \rightarrow Mg^{2+}$ substitution at octahedral sites.

APPROACH

Our approach uses DFT as implemented in the program CASTEP in conjunction with ultrasoft pseudopotentials and plane wave basis functions. The structures of pyrophyllite and of montmorillonite with differing layer charge were determined by energy optimization. The triclinic half unit cell of pyrophyllite $[Si_4Al_2O_{10}(OH)_2]$ was derived from available X-ray diffraction data. A half unit cell of montmorillonite $[Si_4(Al_{1.0} Mg_{1.0})O_{10}(OH)_2]$ with x = 2.0 e (x = layer charge per unit cell) was obtained by substituting one of the octahedral Al^{3+} with Mg^{2+} (Figure 1a). By doubling the structure in Figure 1a, montmorillonite with layer charge x = 1 was created (Figure 1c). An interlayer Na^+ was then added for these two cases (Figures 1b, 1d). Additional simulations were performed by doubling the unit cell with and without Na^+ (x = 0.5; structure not shown). A uniform positively-charged background was used for the cases without Na^+. All CASTEP calculations have been performed on the T3E and IBM SP supercomputers at NERSC.

ACCOMPLISHMENTS

The structure of pyrophyllite determined theoretically was compared with X-ray data and showed excellent agreement in terms of characteristic structural parameters, including tetrahedral rotation angle (10.1 ^{o}), surface corrugation angle (6.7^o), and all interatomic distances. The calculated structures of montmorillonite were compared to pyrophyllite, which is structurally isomorphic to montmorillonite but without charge substitution. For example, the angles of surface corrugation (5°) and tetrahedral rotation (3.4 ^{o}) were less for montmorillonite than for pyrophyllite (Figures 1e, 1f). There was a significant structural effect on the OH groups in the octahedral sheet. Those nearest Na^+ (upper layer in Figure 1b; bottom layer in Figure 1d) moved toward the octahedral sheet and away from the interlayer cation, while the rest (i.e., all other protons in Figures. 1b, 1d) either moved similarly (Figure 1b), or even moved toward the interlayer region (Figure 1d).

SIGNIFICANCE OF FINDINGS

Detailed structural optimization by DFT for pyrophyllite and montmorillonite has been achieved for the first time. Experimentally unavailable but important features such as OH orientation were determined for pyrophyllite (26 ^{o}) and montmorillonite (varying; Figure 1). These quantum mechanical calculations of electronic structure in clay minerals are state-of-the-art and give excellent results for both equilibrium structures and total energies.

Related Publications

Park, S.-H. and Sposito, G. 2001. Methane Hydrate Structure and Stability in Montmorillonite Interlayers. 1. Monte Carlo Simulations. *J. Phys. Chem. B.* (in press).

Park, S.-H. and Sposito, G. 2001. Methane Hydrate Structure and Stability in Montmorillonite Interlayers. 2. Molecular Dynamics Simulations. *J. Phys. Chem. B.* (in press).

Sutton, R. and Sposito, G. 2001. Molecular simulations of interlayer structure and dynamics in 12.4 ÅCs-Smectite hydrates. *J. Colloid Interface Sci.* 237:174-184.

Greathouse, J. A., Refson, K., and Sposito, G. 2000. Molecular Dynamics Simulation of Water Mobility in Magnesium-Smectite Hydrates. *J. Am. Chem. Soc.* 122:11459-11464.

URL: http://esd.lbl.gov/GEO/aqueous_geochem/index.html
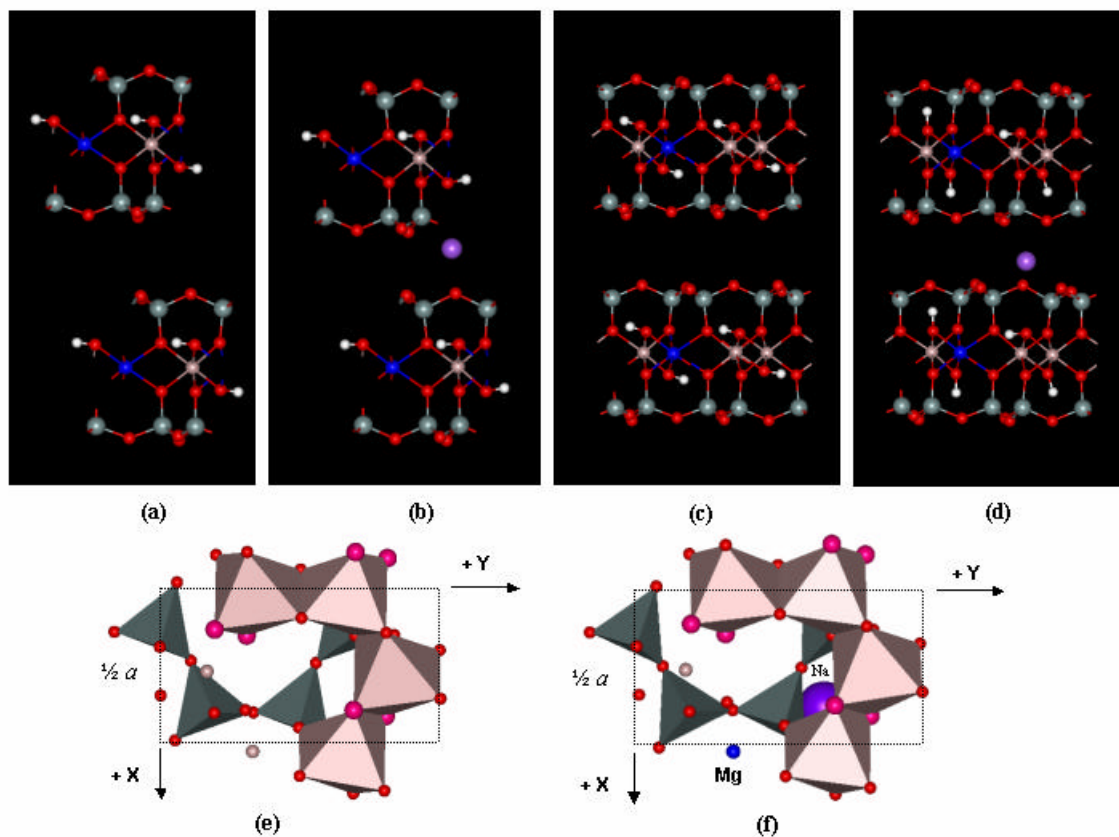
Acknowledgements

Figure 1. (a) to (d) Optimized structure of montmorillonite as determined by ab initio energy minimization based on the local density approximation using gradient-corrected density functional theory. [Si are shown in gray and O are shown in red. The substituted octahedral-sheet cation is Mg^{2+} (blue) and the interlayer cation is Na^+ (purple). Octahedral-sheet Al^{3+} cations are shown in pale red.] Note the positions of the proton (white) and the angle made by OH relative to horizontal. (e) top view of optimized pyrophyllite structure (f) top view of optimized Na-montmorillonite with layer charge = -0.5e.